Rheological Characterization of Energetic Formulations; New Developments

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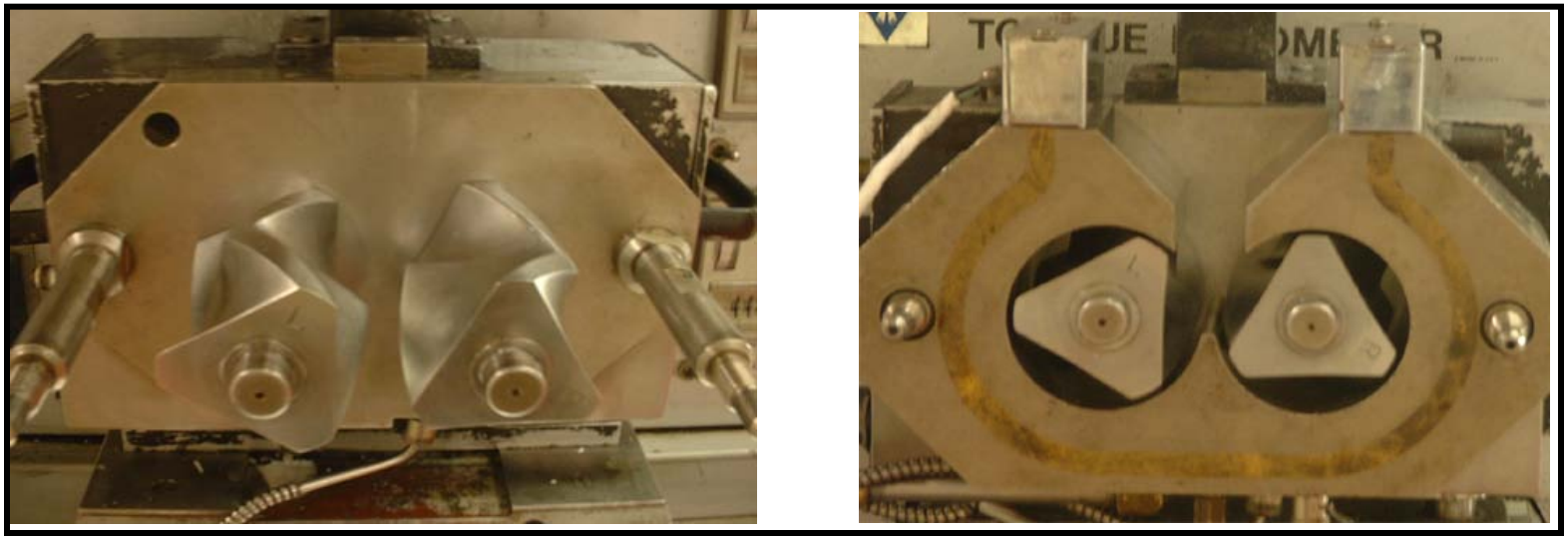
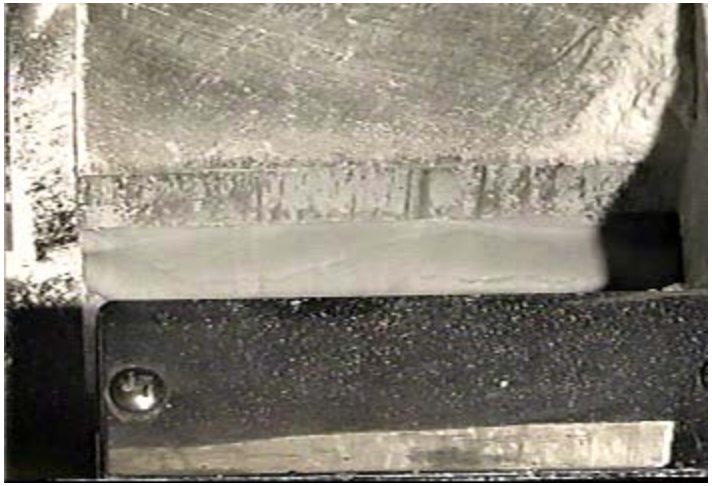
Energetic formulations are complex fluids and present challenges for the characterization of their rheological behavior . These challenges stem from their viscoplasticity and concomitant wall slip behavior.

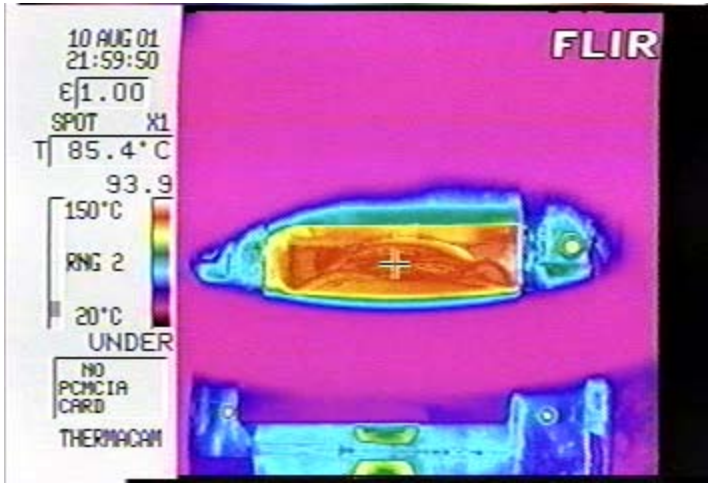
Short Review of the standard tools and their disadvantages

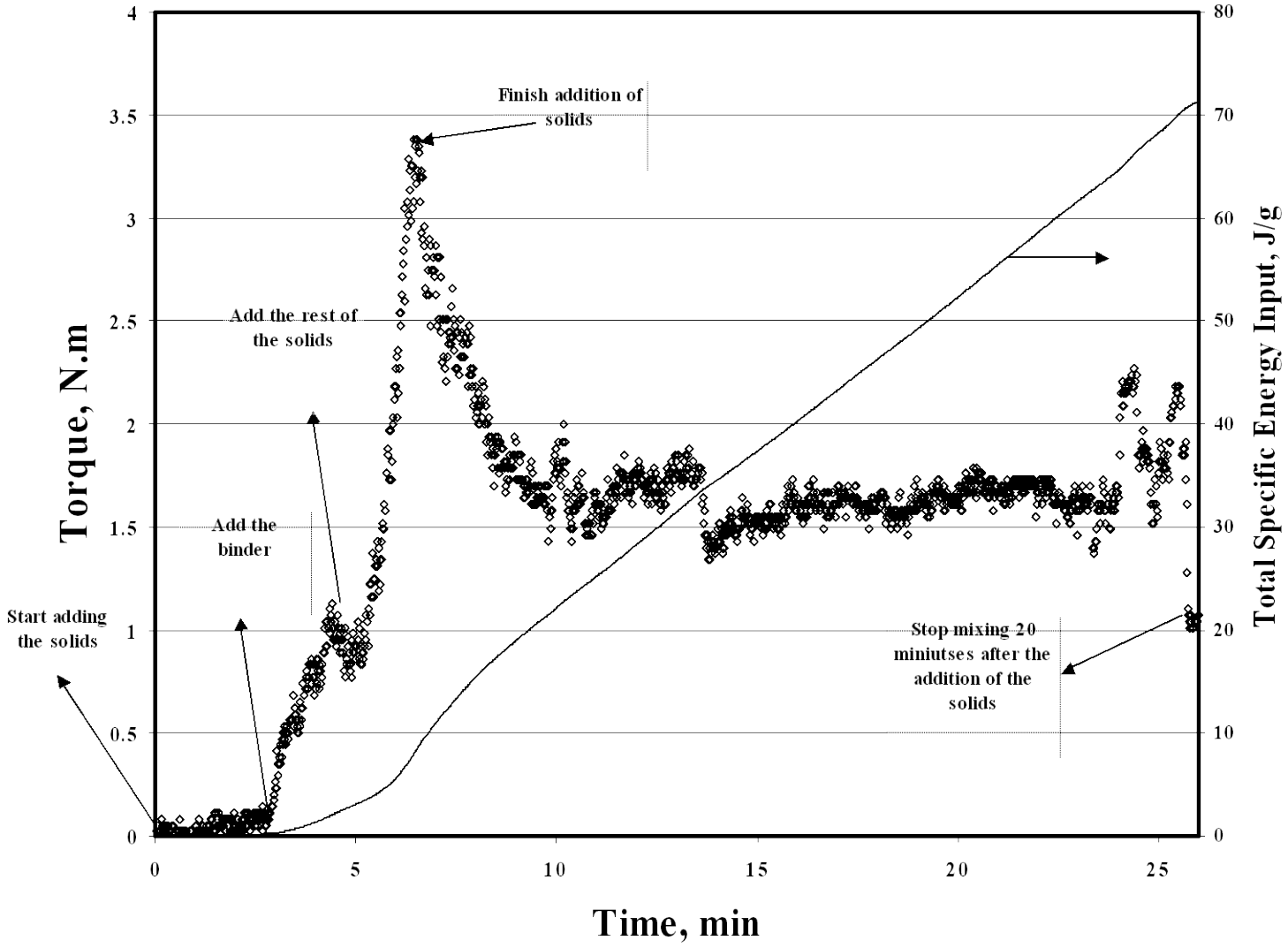
- **Torque Rheometer**
- **Capillary Rheometer**
- **Rotational Rheometer**



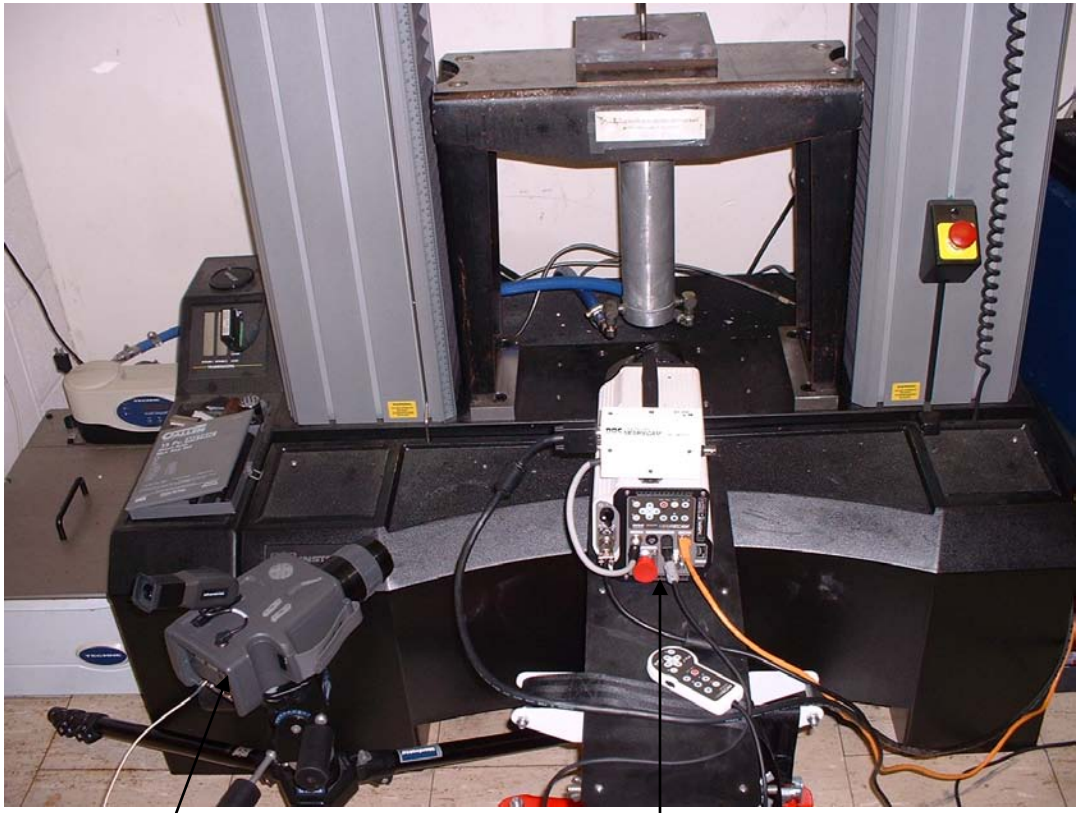
Torque Rheometer/Batch Mixer can be used for preliminary rheological Characterization







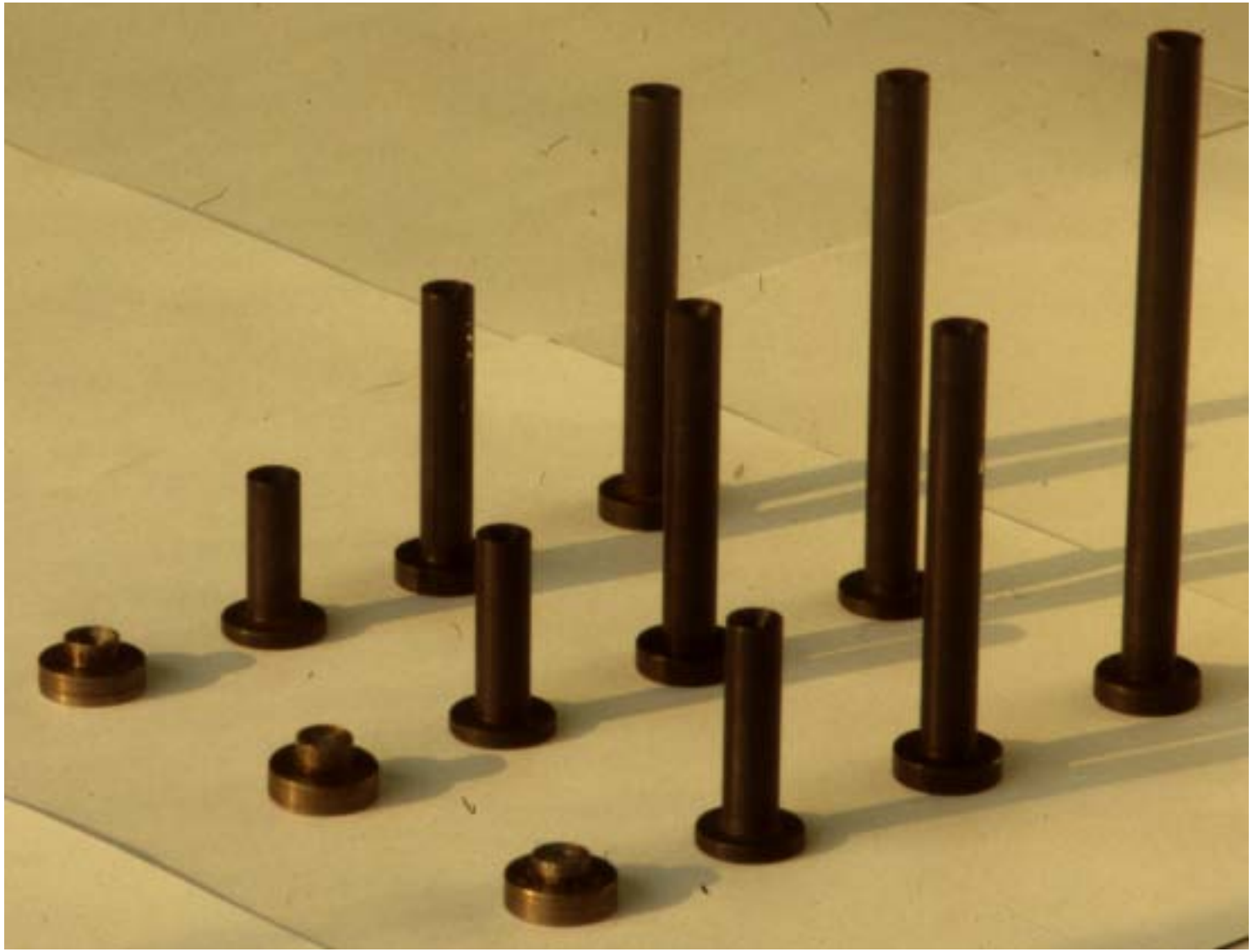
Torque vs. time data at different roller speeds at a given geometry can be used to determine shear viscosity. However the calculated values are very approximate and do not take wall slip into account. Hence, unreliable and too simple for suspensions



Thermal Imaging Camera

High Speed Camera

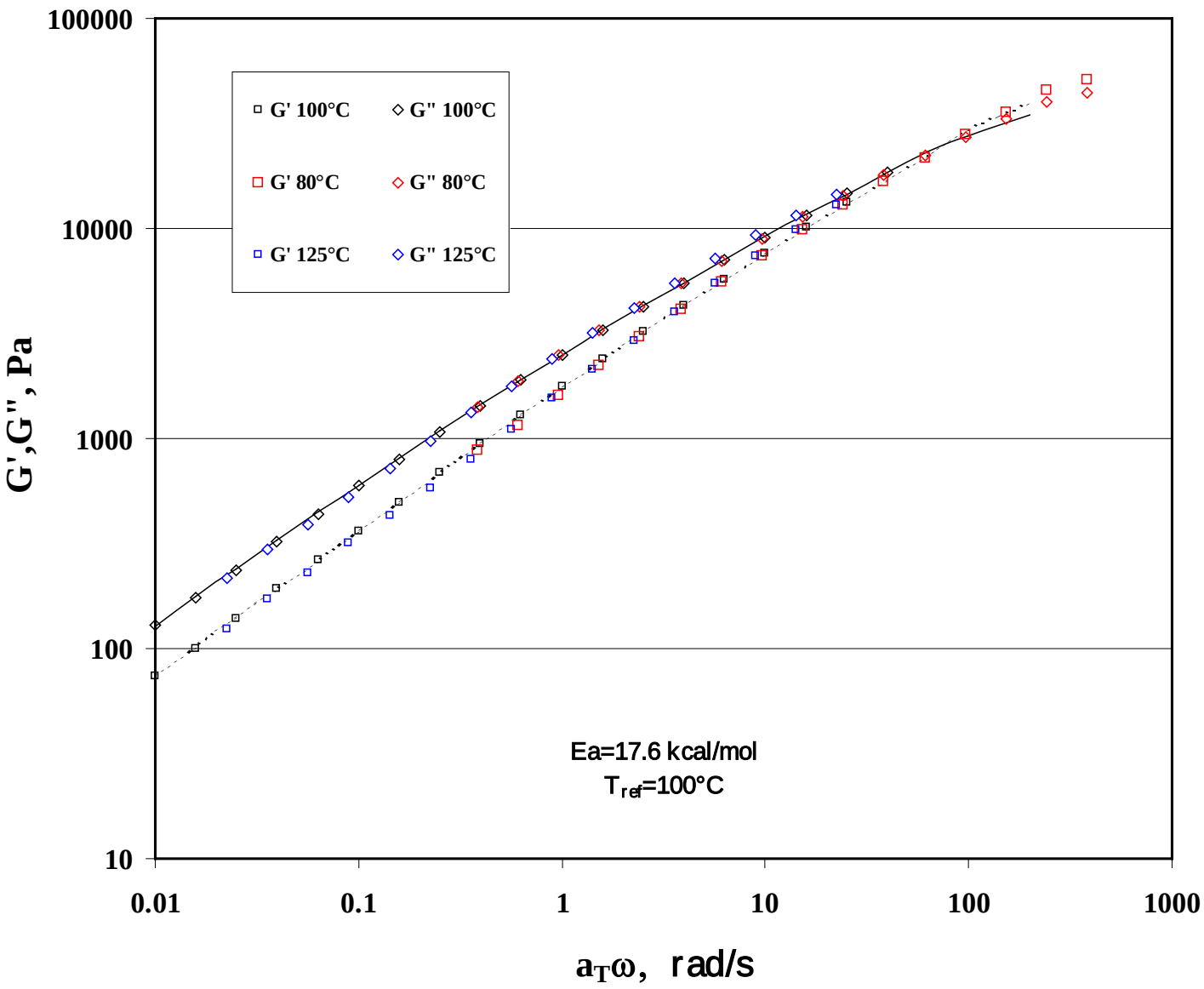
Setup of the Capillary Rheometer together with thermal imaging and high speed cameras



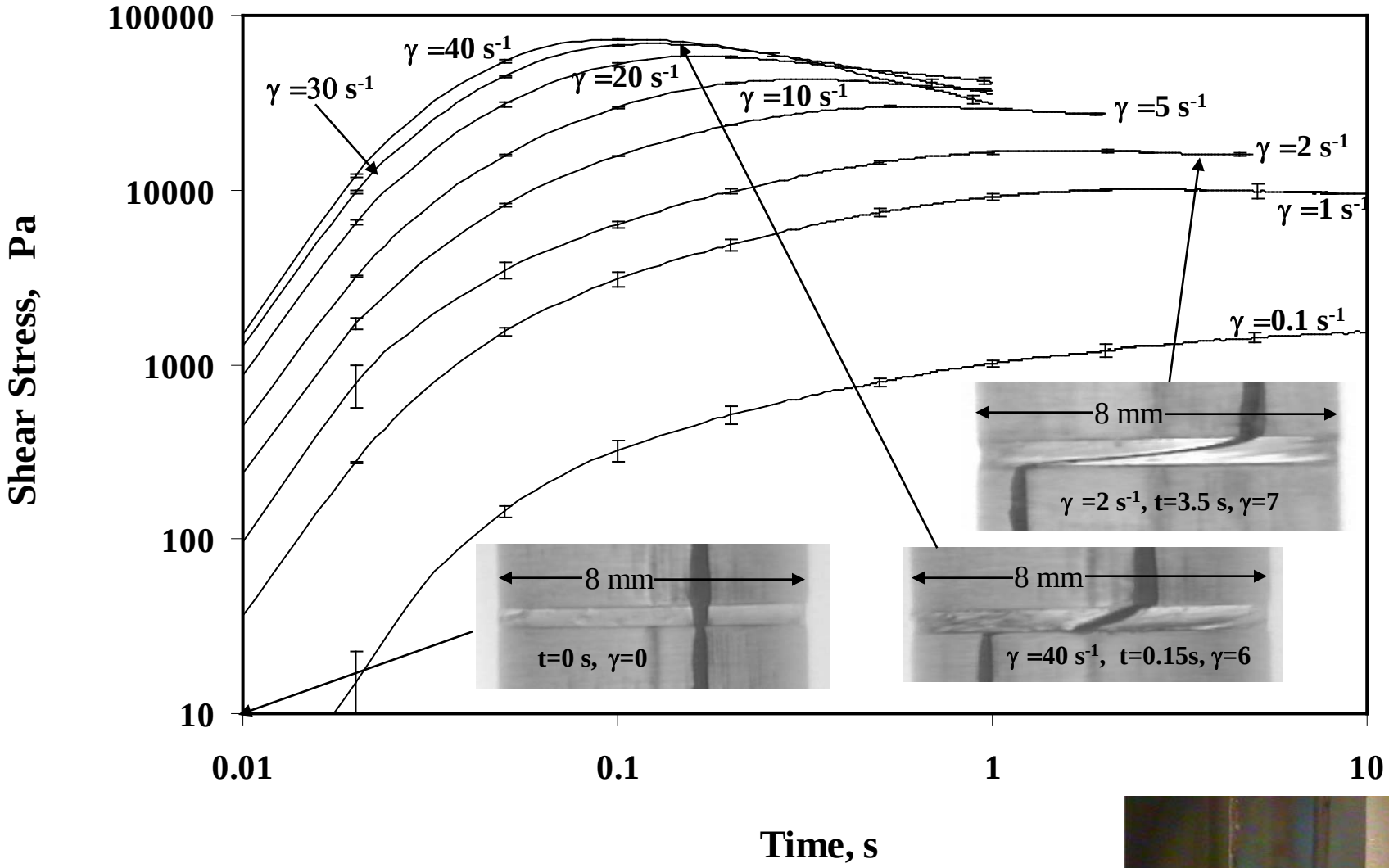
The disadvantage: Need to do too many experiments with multiple capillary dies to get full rheological characterization. Labor intensive and sample loading require human interference, exhibit safety risks

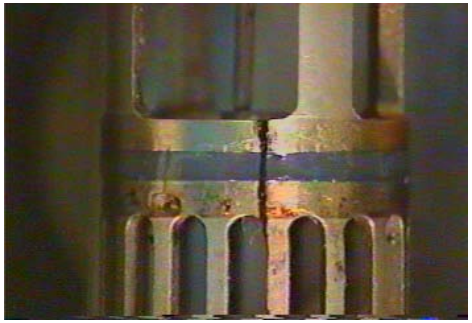
(different L/Ds for Bagley correction, different diameters for wall slip correction)

Rotational Rheometry

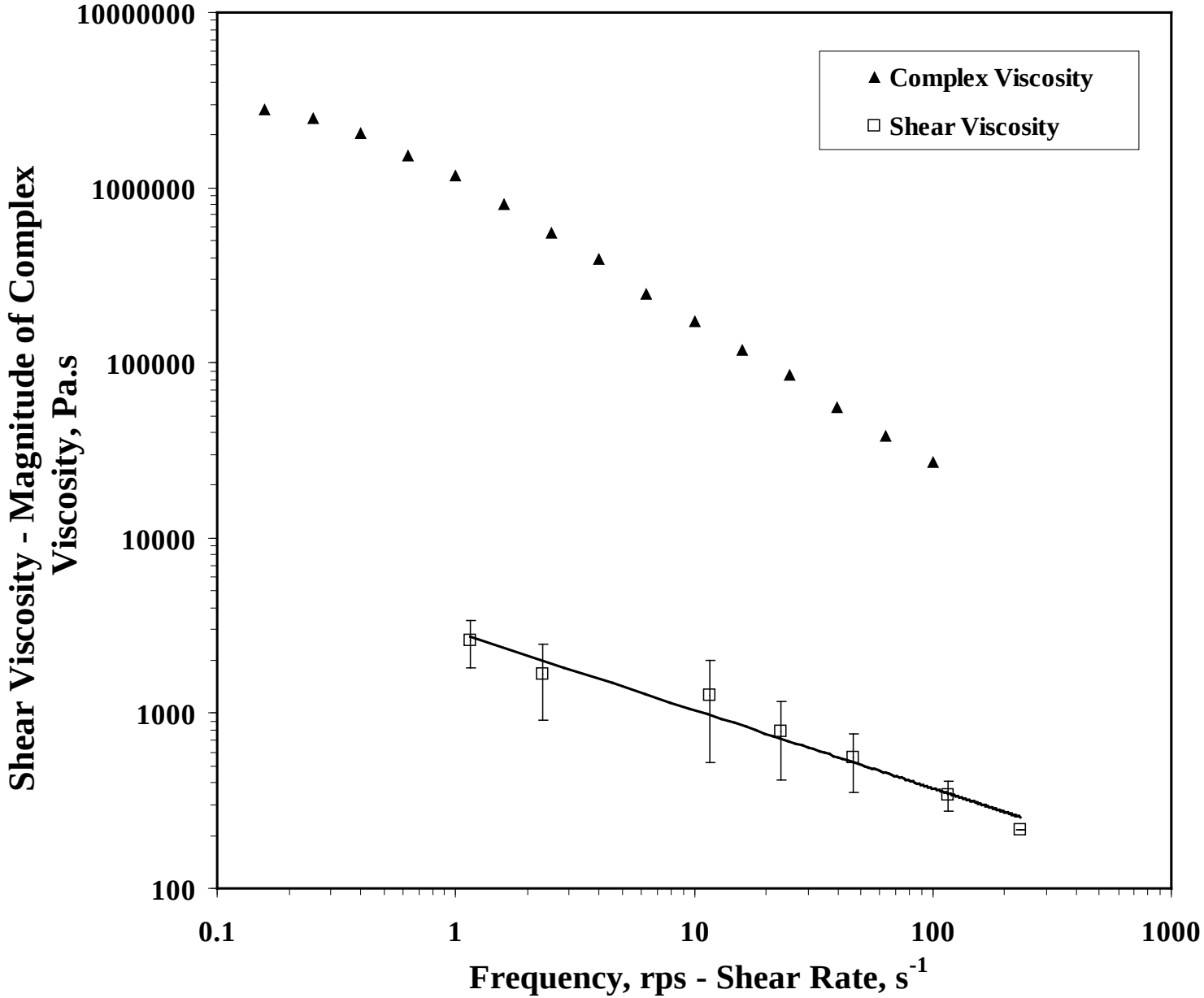


The loss and storage modulus of Bamo-Ammo TPE at various temperatures shifted to the reference temperature of 100°C.





Disadvantages: Measurements primarily limited to low shear rates and subject to wall slip slip

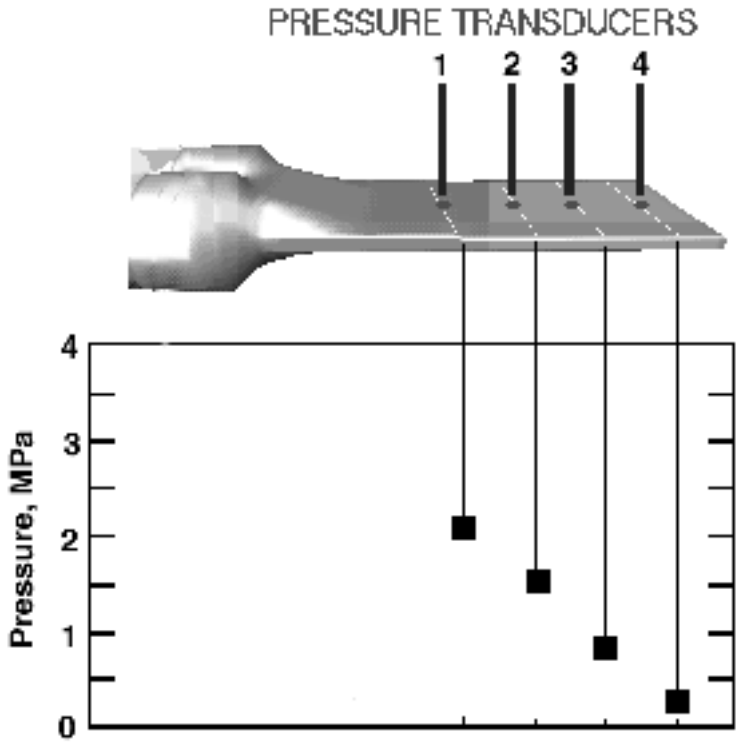


Disadvantage: Shear viscosity and Magnitude of complex viscosity do not match for filled systems, unlike simple polymers.

What are better alternatives:

- **On-line Adjustable Rectangular Slit Rheometer**
- **Off-line Adjustable Rectangular Slit Rheometer**
- **Squeeze flow Rheometer**
- **Or their combination together with the FEM based inverse solution of these flows.**

ADJUSTABLE GAP RHEOMETER



Pressure versus distance in the die

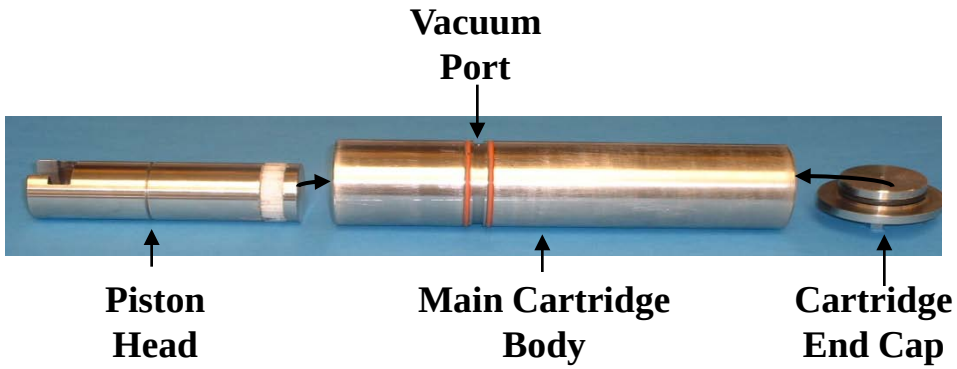
Ability to alter the flow rate and the gap of the slip independently provides the basic platform for slip correction

On-line Adjustable Slit Rheometer:

- **Attaches to an extruder, no need for material loading**
- **No entrance correction**
- **Change surface area to volume ratio by the infinitely adjustable the slit opening**
- **Ability to apply vacuum on the extruder side (if required).**
- **Require minimal user interference.**

Off-line Slit Rheometer:

- No entrance correction
- Change surface area to volume ratio by the infinitely adjustable the slit opening
- Very good control on the flow rate, free of disturbances associated with upstream operation of a continuous extruder system



Bi-directional Hydraulic Cylinder that enables movement in horizontal direction

Collar that hold the cartridge in place as the piston moves vertically

Piston Head

Cartridge is inserted into the circulation block

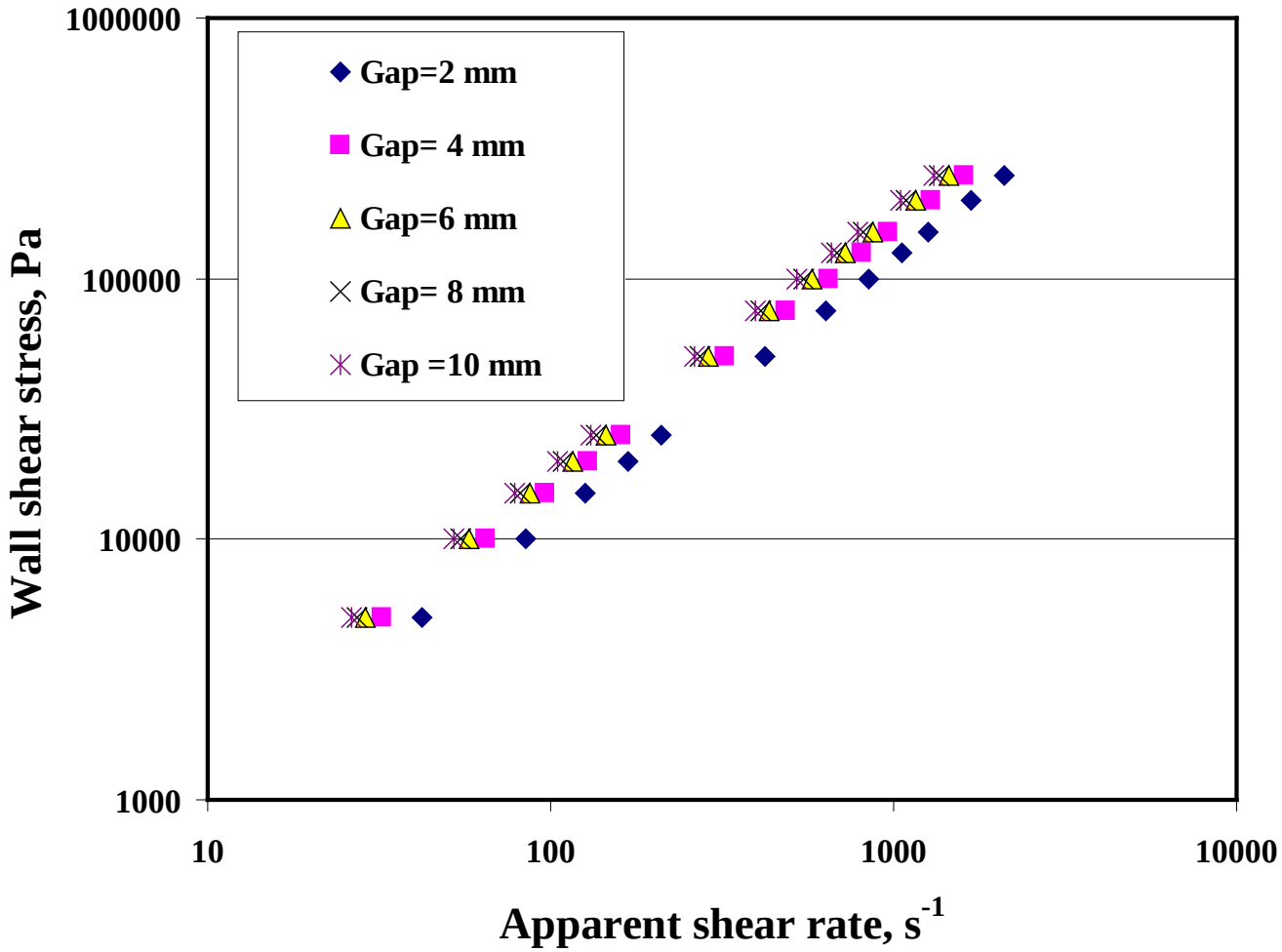
Vacuum Port on fill station

Hand Pump

Circulation Block in which the cartridge assembly sits in

Off-line Slit Rheometer Fill Station:

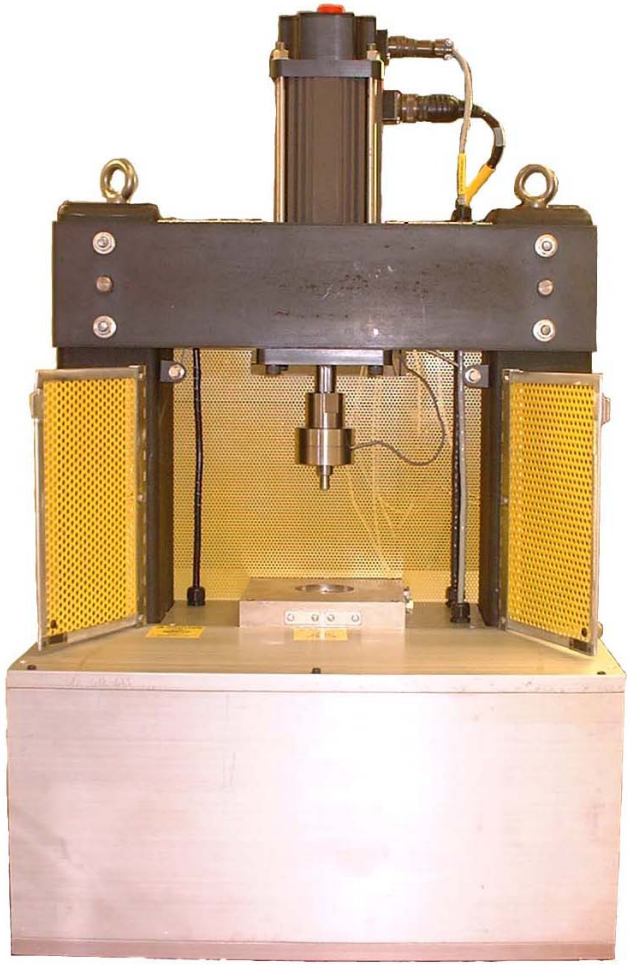
- Ability to apply vacuum during cartridge loading
- The fill station is operable remotely if safety is an issue.

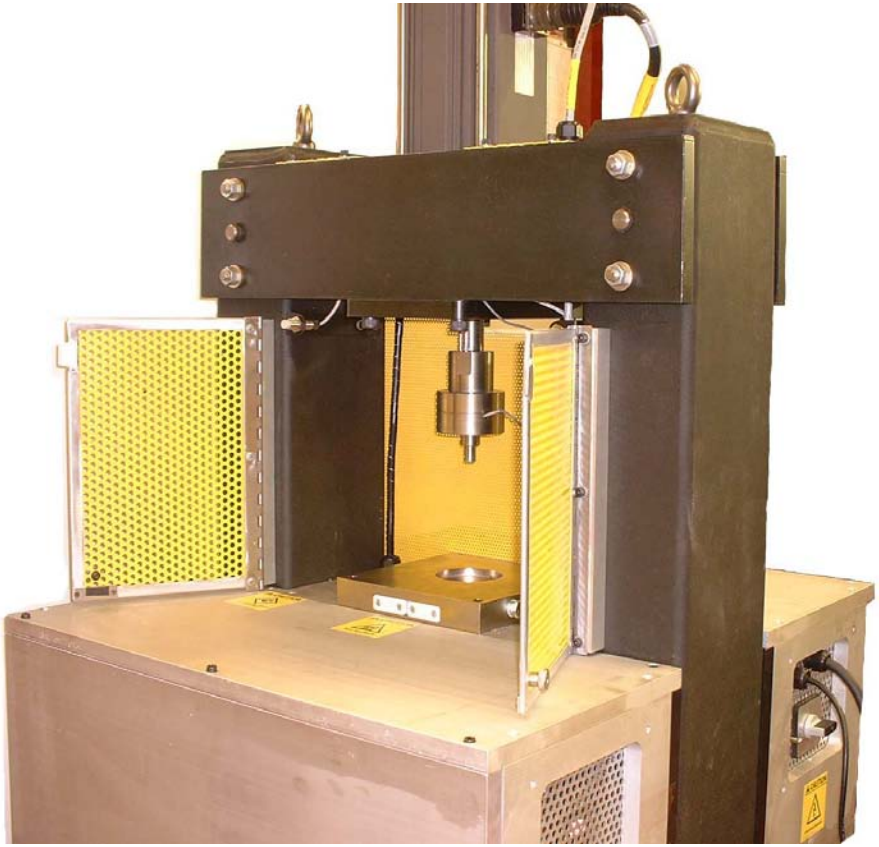


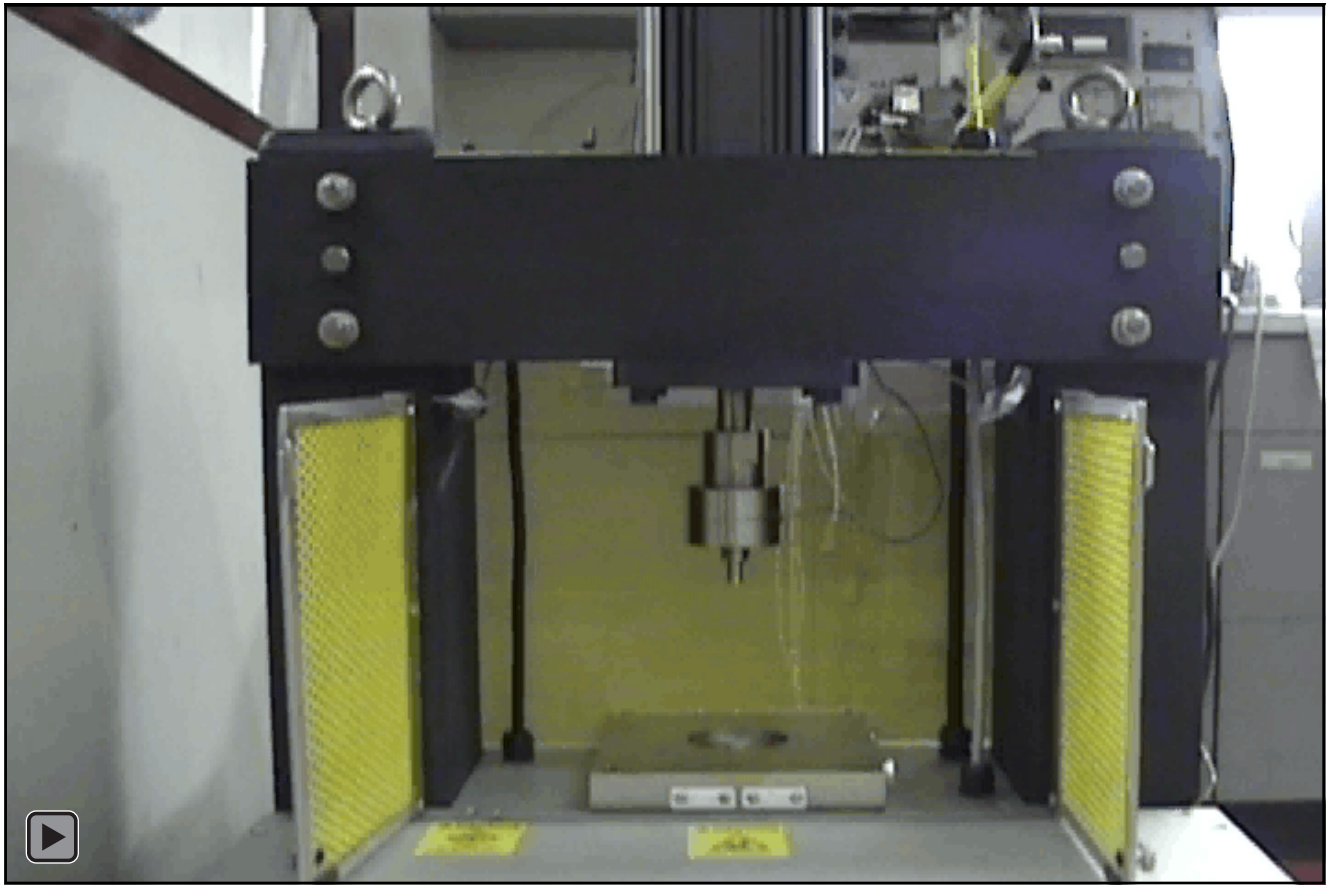
The wall shear stress is lower at smaller gap openings due to the larger surface area to volume ratios and hence wall slip

New Generation of Squeeze Flow Rheometer

- Can apply up to 5000 lbf load.
- Use a servo motor to control the ram speed accurately over a wide range (0.01-200 in/min)
- Option to run remotely, with no operator present during the characterization, with minor modifications
- Temperature controlled material platform
- Capability of measuring various types of data; including force, gap, velocity, and material platform temperature

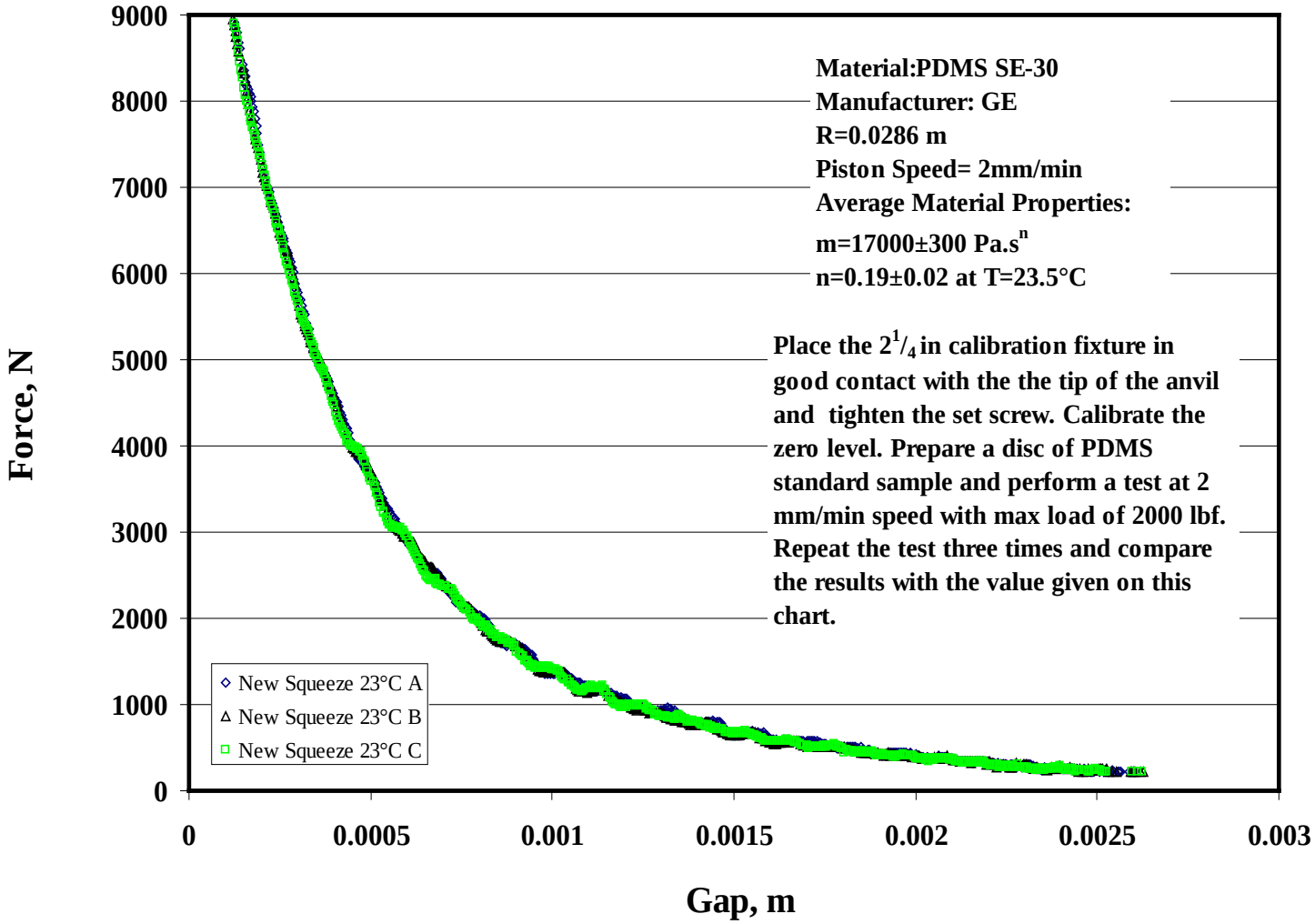






Advantages of Squeeze Flow Rheometer

- **Possible to collect data over a wide range of shear rate in one test**
- **Plug flow condition due to pure slip will be always avoided and the sample is always guaranteed to be deformed, which is usually a problem in viscometric flows of highly filled suspensions**
- **Squeeze flow provides significant advantages in safety of materials handling and exposure as well as providing easy data generation for routine quality control of energetic formulations being processed.**
- **Analytical and numerical analyses can be used for the solution of the inverse problem of squeeze flows to characterize the shear viscosity and the wall slip parameters.**



Get material parameters reproducibly by a relatively simple analytical method

Estimation of the Parameters of Herschel-Bulkley Fluid under Wall Slip Using a Combination of Capillary, Slit and Squeeze Flow Viscometers

Advantages:

Using a combination of these test will reduce the number of experiments significantly without compromising on the quality of the final results with additional safety features.

Governing Equations used for the solution squeeze flow problem

$$\tau_{rz} = \pm\tau_y - m\,|\,dv_r/dz\,|^{n-1}\,(dv_r/dz)$$

$$U_s = \beta\ |\tau_{rz}|^{sb},$$

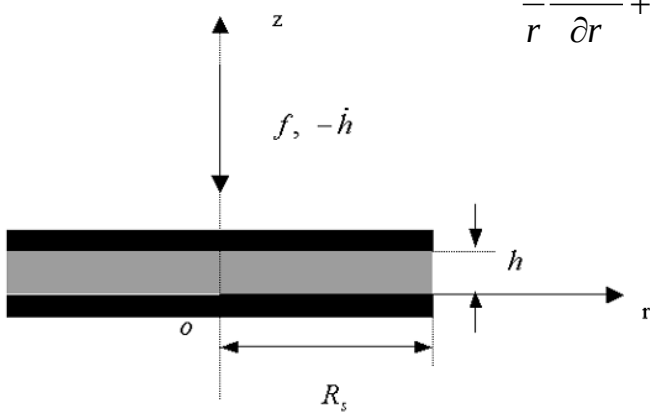
Material Properties that we want to solve for.

$$\frac{1}{r}\frac{\partial r v_r}{\partial r} + \frac{\partial v_z}{\partial z} = 0$$

$$\frac{1}{r}\frac{\partial r\tau_{rr}}{\partial r} + \frac{\partial \tau_{rz}}{\partial z} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial p}{\partial r} = 0,$$

$$\frac{1}{r}\frac{\partial r\tau_{rz}}{\partial r} + \frac{\partial \tau_{zz}}{\partial z} + \frac{\partial p}{\partial z} = 0.$$

Continuity and momentum equations

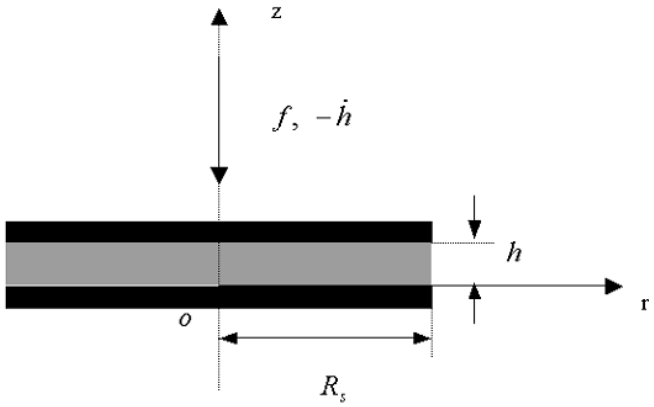


Experimental:

Test with PDMS, and its suspensions with rigid spherical particles. The particles were hollow glass spheres obtained from Potters Industries with a specific gravity of 1.09, arithmetic particle diameter of 12 μm and a maximum packing fraction of 0.65. With squeeze flow rheometer ram diameter of 0.0572 m with top plate velocities of, $2.1*10^{-4}$ m/s, $4.2*10^{-4}$ m/s and $8.4*10^{-4}$ m/s. On the other hand, for capillary flows, capillaries with diameters of $2.5*10^{-3}$ and $1.5*10^{-3}$ m were employed at a constant length over the diameter ratio of 40. All of the experiments were carried out under ambient temperature

Squeeze flow is used in conjunction with the **capillary** and /or **slit flow** data to provide the data necessary for the **solution of the inverse problem** to characterize the three **parameters of the Hershel-Bulkley equation** and the two **parameters of the wall slip velocity** versus wall shear stress relationship.

Experimental data from squeeze flow consist of the normal force acting on the top surface, which is the driving force for the flow, f_1^e, f_2^e, f_3^e… f_{Ms}^e, at gap (or distance of separation between the two plates) $h_1, h_2, h_3 \ldots h_{Ms}$, respectively. The data from the capillary flow would be the flow rates or the corresponding apparent shear rates at γ_{a1}, γ_{a2}, γ_{a3}… γ_{aMs} and the Bagley corrected wall shear stress values of $\tau_{w1}, \tau_{w2}, \tau_{w3}$… τ_{wMs}, respectively. The parameter estimation problem can be formulated as the following inverse problem:



$$Find \quad \{m, n, \tau_y, \beta, sb\} = \{m, n, \tau_y, \beta, sb \mid J(F, \Gamma, F^e, \Gamma^e)$$

$$= \min_{m,n,\tau_y,\beta,sb} J(F, \Gamma, F^e, \Gamma^e)\},$$

where the objective function is defined as

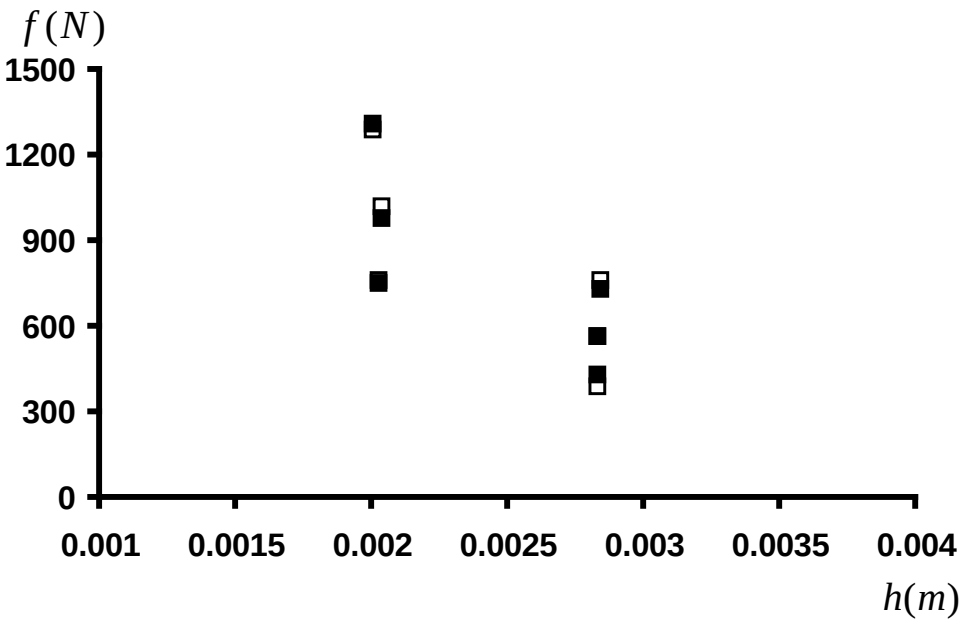
$$J(F,\Gamma,F^e,\Gamma^e) = \kappa\left(\frac{1}{M_s}\sum_{i=1}^{M_s}(1-\frac{f_i}{f_i^e})^2 + \frac{1}{M_s-1}\sum_{i=1}^{M_s-1}(1-\frac{f_{i+1}-f_i}{f_{i+1}^e-f_i^e})^2\right)$$
$$+(1-\kappa)\left(\frac{1}{M_c}\sum_{i=1}^{M_c}\left(1-\frac{\dot{\gamma}_{ai}}{\dot{\gamma}_{ai}^e}\right)+\frac{1}{M_c-1}\sum_{i=1}^{M_c-1}\left(1-\frac{\dot{\gamma}_{ai+1}-\dot{\gamma}_{ai}}{\dot{\gamma}_{ai+1}^e-\dot{\gamma}_{ai}^e}\right)^2\right).$$

Here, $0<\kappa<1$,$F=\{f_1, f_2 \ldots f_M\}$, $\Gamma=\{\gamma_{a1}, \gamma_{a2}, \ldots \gamma_{aMs}\}$, $F^e=\{f_1^e, f_2^e \ldots f_M^e\}$ and $\Gamma^e=\{\gamma_{a1}^e, \gamma_{a2}^e, \ldots \gamma_{aMs}^e\}$. F values are the computed values of the forces acting on the top plate to drive the flow during squeeze flow and F^e values are the experimental force values as a function of time during the squeeze flow. F values can be computed upon the integration of the pressure and normal stress distributions in the radial direction. When $0<\kappa<1$, the objective function J is defined here as a weighted function of squeeze flows and capillary flows. In the estimation, both squeeze and capillary flows are used, i.e., κ=0.5.

How are we going to solve this complex problem?

➢It can be solved numerically using the Finite Elements Method. Our numerical method employs a Galerkin/penalty finite element approach with bilinear rectangular elements. The error minimization involves nonlinear iterations that are carried out using the deepest descent method for the first few iterations and then adopting the conjugate gradient method for the rest of the iterations

➢The estimation using squeeze, capillary-slit flows may suffer from non-uniqueness, and the solution upon minimization is dependent on the initial guess when the number of parameters being sought exceeds two. To overcome the problem and obtain the solution pertaining to a global minimum, a new procedure is proposed. Define possible upper and lower bounds for m, n, τ_y, β and s_b and search within this window.



$h_i\,(mm)$	$f_i^e\,(N)$
5.7	13
3.4	16
2.3	22
1.5	34
1.19	50
0.95	71
0.69	123
0.59	164
0.43	298
0.31	564
0.25	863
0.21	1223
0.18	1668
0.16	2014
0.15	2413

$m = 17200 Pa \cdot s^{0.39}$,

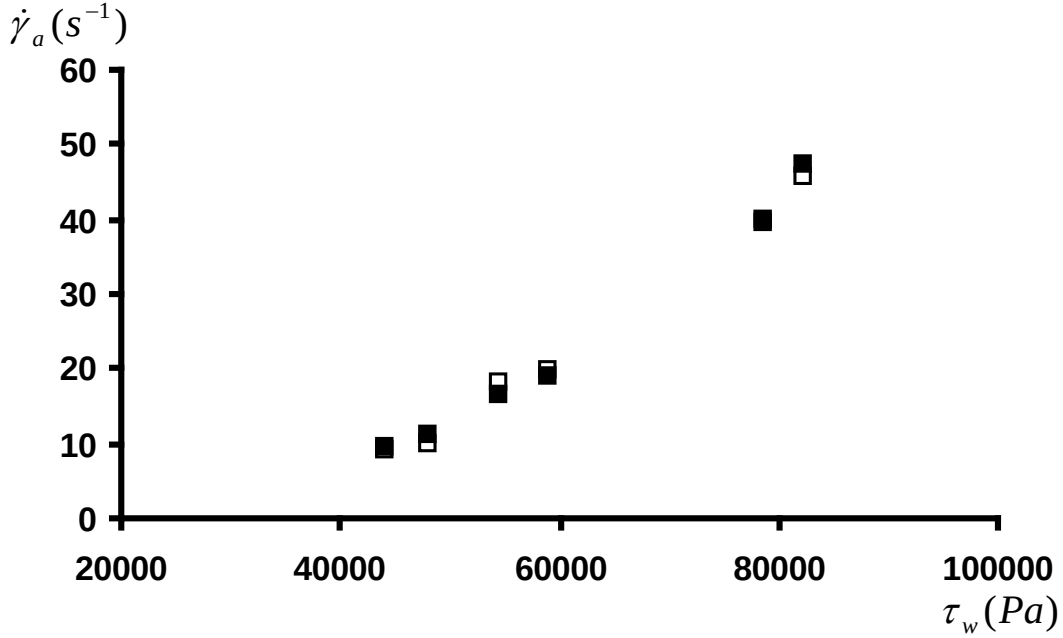
$n = 0.39$,

$\tau_y = 0 Pa$,

$\beta = 8.3 \times 10^{-15} m \cdot s^{-1} \cdot Pa^{-2.26}$,

$sb = 2.26$.

Predicted and experimentally obtained gap versus force data of squeeze flow for pure PDMS at three different ram speeds. Filled squares are computed values and hollow squares are experimental data. All five parameters are calculated using both squeeze and capillary flows simultaneously (κ=0.5).



$\dot{\gamma}_{ai}(s^{-1})$	$\tau_{wi}{}^{e}(Pa)$
5.5	6000
10.5	10000
18.6	15000
29.3	20000
153.9	50000
397.8	80000
932.4	120000
1503.3	150000
3446.1	220000
6790.1	300000

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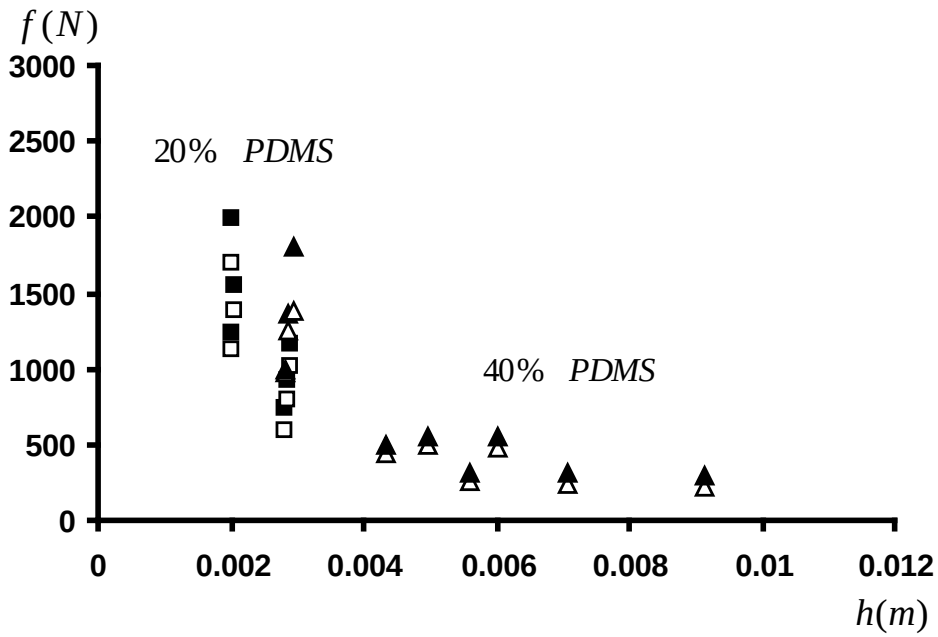
Predicted and experimentally obtained apparent shear rates and wall stresses of capillary flow for pure PDMS. Filled squares are computed values and hollow squares are experimental data. All five parameters are calculated using both squeeze and capillary flows simultaneously (κ=0.5).



20% Glass filled PDMS

$m = 33900 Pa \cdot s^{0.32}$,

$n = 0.32$,

$\tau_y = 10 Pa$,

$\beta = 3.6 \times 10^{-14} m \cdot s^{-1} \cdot Pa^{-2.165}$,

40% Glass filled PDMS

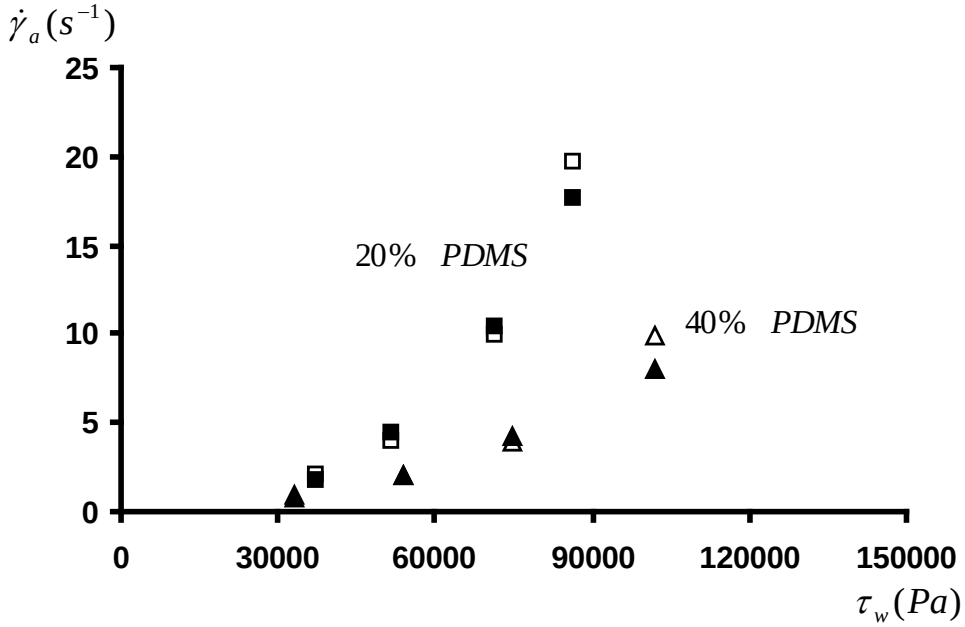
$m = 50000 Pa \cdot s^{0.5}$,

$n = 0.50$,

$\tau_y = 403 Pa$,

$\beta = 2.1 \times 10^{-14} m \cdot s^{-1} \cdot Pa^{-2.165}$.

Predicted and experimentally obtained gaps and forces of squeeze flow for 20% and 40% by volume PDMS. Filled symbols – computation, hollow symbols– experiment. The data were obtained upon the use of multiple plate velocities. The slip layer consists solely of pure PDMS and thus, the exponent in the slip velocity versus the wall shear stress relationship is determined a priori as s_b=2.165 . The set of the other unknown four parameters were obtained upon the solution of the inverse problem by employing both squeeze and capillary flows.



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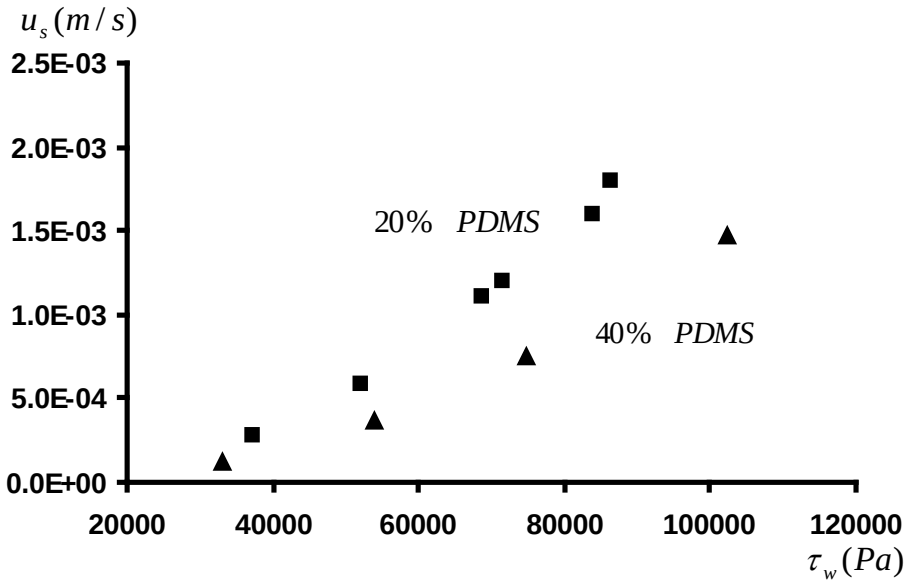

Predicted slip velocity for 20% and 40% by volume PDMS.

Conclusions:

- Minimizing human interference during rheological characterization is advantageous using slit and squeeze flow rheometers.
- Using a combination of these test, in conjunction with the their inverse FEM analysis is a good alternative to conventional methods.
- The capacity of the method to identify the parameters is investigated. It is shown that it is easier to obtain a unique solution when the number of unknowns is 2 or 3, but it is difficult to determine all of the five parameters.
- The combination of the data emanating from squeeze and capillary flows versus the use of data from either the capillary or the squeeze flow provides a more reliable estimation.
- The division of the solution domain into a large number of subdomains, over which the local minima are computed to allow the global minimum to be determined, is an important part of the procedure.